The Perturbed Hyperfine Structure of the $3s^2 3d\ ^2D$- and $3s^2 4d\ ^2D$-States of Al I

B. Falkenburg and P. Zimmermann
Institut für Strahlungs- und Kernphysik
der Technischen Universität Berlin

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The influence of interconfiguration interaction between the nd ^2D-series and the $3s3p^2$ configuration in Al I with regard to the magnetic hyperfine structure of the $3s^2 3d\ ^2D$- and $3s^2 4d\ ^2D$-states is discussed.

Introduction

The lowest $3s^2 nd\ ^2D_{3/2,\,5/2}$-states in the nd ^2D-series of Al I show some remarkable irregularities: The fine structure splitting δW, which in the one electron approximation should vary as n^{*-3} (n^* effective quantum number), strongly deviates for the first members. A similar irregular behaviour is displayed by the values of the oscillator strength $f(3p\text{-}nd)$ for the electric dipole transitions ot the ground state 3p.

Obviously, these anomalies are caused by interconfiguration interactions. As in the Al sequence (Si II, P III, S IV, etc.) there is a strong interaction between the $3s^2 3d\ ^2D$ and the $3s3p^2\ ^2D$, one should also try to explain the perturbation in the $3s^2 nd\ ^2D$-series in Al I by the interaction with the $3s3p^2\ ^2D$-states. The solution of this problem is of special interest because the position of the $3s3p^2\ ^2D$ is still unknown.

In an earlier paper Paschen [1] suggested that the $3s^2 3d\ ^2D$ should be replaced by the $3s3p^2\ ^2D$ because of the extremely small fine structure splitting $\delta W = 1.34\ \mathrm{cm}^{-1}$. This classification seemed to be confirmed by an analysis of hyperfine and mean lifetime values of the $3d\ ^2D_{5/2}$ measured with the level crossing technique [2]. On the other hand, Stark effect measurements [3] showed that the complete replacement of the $3s^2 3d\ ^2D$ by the $3s3p^2\ ^2D$ was unlikely because the large Stark shifts of the $3s^2 3d\ ^2D$-states could very well be explained by admixtures of the approximate $3s^2 4p\ ^2P$-states, whereas these admixtures would be prohibited in the case of the $3s3p^2\ ^2D$.

From the anomalous behaviour of the f-values, Grudzev [4] concluded that instead of the $3s^2 3d\ ^2D$ the $3s^2 4d\ ^2D$ should be replaced by the $3s3p^2\ ^2D$. However, as in the case of the $3s^2 3d\ ^2D$, Stark effect measurements [5] confirmed the classification $3s^2 4d\ ^2D$ because the large Stark shifts of these states are mainly due to admixtures of the $3s^2 5p\ ^2P$-states, which cannot be mixed by an electric field to the $3s3p^2\ ^2D$-states.

From a theoretical point of view a satisfactory answer to these questions concerning the unknown position of the $3s3p^2\ ^2D$ was given by calculations of Weiss [6], who showed that the $3s3p^2\ ^2D$ is strongly coupled to all members of the $3s^2 nd\ ^2D$-series; i.e. it is smeared out over the entire series thereby losing its identity. Weiss checked his wave functions by calculating the f-values of the transitions nd-3p ($n = 3-7$) and obtained excellent agreement with the experimental values. From the dominant composition of the five lowest nd ^2D-states given in his paper, one can see that all these states have large admixtures of the $3s3p^2\ ^2D$.

Hyperfine Structure

Another important test for the wave functions of the ^2D-states is the analysis of the hyperfine structure. In fact, this test is complementary to the calculation of f-values, because for the calculation of the hyperfine constants the inner part of the wave function near the nucleus is most important, whereas for the f-values the wave function outside the core is decisive. The magnetic hyperfine splitting, which is caused by the interaction of the magnetic field of the electrons at the nucleus with the nuclear magnetic moment, can be very sensitive so small changes in the electronic wave functions. This is especially true for the mixing of configurations with unpaired s-electrons like the $3s3p^2$-configuration because of their large contributions to the magnetic hyperfine constant A. Admixtures of these configurations can drastically change the value of A of the unperturbed states.

At first, it is necessary to look at the experimental values of the A-factors of the $3s^2 3d\ ^2D$- and $3s^2 4d\ ^2D$-states, which were determined by the

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Reprint requests to Prof. Dr. P. Zimmermann, Institut für Strahlungs- und Kernphysik der Technischen Universität Berlin, Rondellstr. 5, D-1000 Berlin 37.

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level-crossing technique [2, 3, 5]:

$$A\,(3\mathrm{s}^2 3\mathrm{d}\ {}^2\mathrm{D}_{5/2}) = 182\ \mathrm{MHz},$$
$$A\,(3\mathrm{s}^2 3\mathrm{d}\ {}^2\mathrm{D}_{3/2}) = -100\ \mathrm{MHz},$$
$$A\,(3\mathrm{s}^2 4\mathrm{d}\ {}^2\mathrm{D}_{5/2}) = 204\ \mathrm{MHz},$$
$$A\,(3\mathrm{s}^2 4\mathrm{d}\ {}^2\mathrm{D}_{3/2}) = -\ 74\ \mathrm{MHz}.$$

For several reasons it is quite obvious, that these A-factors are the result of perturbations:

- the A-factors of unperturbed 3d and 4d electrons should have the same sign, i.e. positive for the positive magnetic moment of Al^{27}.
- their ratio should be $A\,(n\mathrm{d}\ {}^2\mathrm{D}_{5/2})/A\,(n\mathrm{d}\ {}^2\mathrm{D}_{3/2}) = 3/7$.
- their values should be at least by one order of magnitude smaller than the experimental values.

Then one should consider the theoretical A-factors of the ^{2}D-states of the $3\mathrm{s}3\mathrm{p}^2$-configuration which in the nonrelativistic limit are given by

$$A\,(3\mathrm{s}3\mathrm{p}^2\ {}^2\mathrm{D}_{5/2}) = 0.8 a_{3\mathrm{p}} + 0.2 a_{3\mathrm{s}}\,,$$
$$A\,(3\mathrm{s}3\mathrm{p}^2\ {}^2\mathrm{D}_{3/2}) = 1.2 a_{3\mathrm{p}} - 0.2 a_{3\mathrm{s}}\,.$$

Contrary to the A-factors of the single 3d- or 4d-electrons, these A-factors change sign between the $^2\mathrm{D}_{5/2}$- and $^2\mathrm{D}_{3/2}$-states because of the large value $a_{3\mathrm{s}}$ of the unpaired 3s-electron. Admixtures of these wave functions to the nd ^{2}D should appreciably change the values of the A-factors of the unperturbed states. In fact, regarding the small values of $a_{n\mathrm{d}}$, the A-factors should mainly be determined by just these admixtures. In the paper of Weiss, the dominant composition of the ^{2}D wave functions in terms of the transformed superposition-of-configuration (SOC) functions is:

$$|3\mathrm{s}^2 3\mathrm{d}'\rangle = 0.8561\,|3\mathrm{s}^2 3\mathrm{d}\rangle + 0.4605\,|3\mathrm{s}3\mathrm{p}^2\rangle - 0.1708\,|3\mathrm{p}^2({}^1\mathrm{D})3\mathrm{d}\rangle - 0.0929\,|3\mathrm{p}4\mathrm{p}({}^1\mathrm{S})3\mathrm{d}\rangle\,,$$

$$|3\mathrm{s}^2 4\mathrm{d}'\rangle = 0.8543\,|3\mathrm{s}^2 4\mathrm{d}\rangle - 0.4609\,|3\mathrm{s}3\mathrm{p}^2\rangle - 0.1787\,|3\mathrm{p}^2({}^1\mathrm{D})4\mathrm{d}\rangle - 0.0974\,|3\mathrm{p}4\mathrm{p}({}^1\mathrm{S})4\mathrm{d}\rangle\,.$$

For the calculation of the single electron parameters a_{nl} we used the radial functions obtained by the parametric potential method [7]. For the main contributions $a_{3\mathrm{s}}$ and $a_{3\mathrm{p}}$ the following values were obtained:

$$a_{3\mathrm{s}} = 3240\ \mathrm{MHz} \quad \text{and} \quad a_{3\mathrm{p}} = 152\ \mathrm{MHz}.$$

With these values the A-factors of the perturbed $3\mathrm{s}^2 3\mathrm{d}'\ {}^2\mathrm{D}$- and $3\mathrm{s}^2 4\mathrm{d}'\ {}^2\mathrm{D}$-states were calculated:

$$A\,(3\mathrm{s}^2 3\mathrm{d}'\ {}^2\mathrm{D}_{5/2}) = 180\ \mathrm{MHz},$$
$$A\,(3\mathrm{s}^2 3\mathrm{d}'\ {}^2\mathrm{D}_{3/2}) = -104\ \mathrm{MHz},$$
$$A\,(3\mathrm{s}^2 4\mathrm{d}'\ {}^2\mathrm{D}_{5/2}) = 196\ \mathrm{MHz},$$
$$A\,(3\mathrm{s}^2 4\mathrm{d}'\ {}^2\mathrm{D}_{3/2}) = -\ 81\ \mathrm{MHz}.$$

The comparison with the experimental values is quite satisfactory. It seems, therefore, that the wave functions of Weiss are quite suitable to describe the physical state of 3d and 4d in Al I.

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